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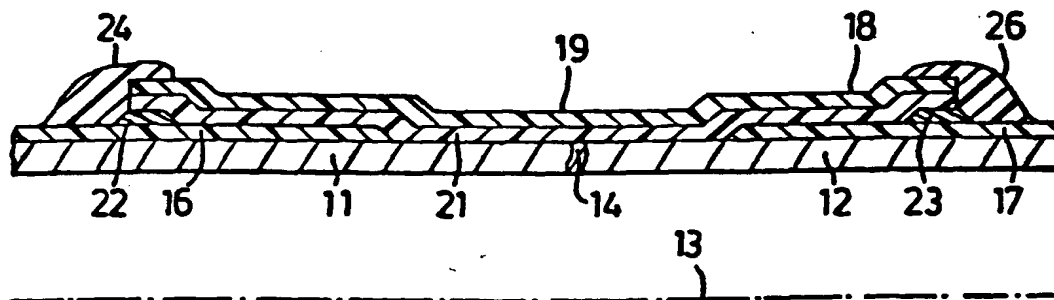
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(54) Title: SLEEVE FOR PROTECTING POLYPROPYLENE-COVERED PIPE COMPRISING BONDING AGENT



(57) Abstract: An elongate tubular article extending along a longitudinal axis has a polypropylene covering. A polyolefin secondary covering is at least partially superimposed over the polypropylene. The secondary covering has an edge with a face extending transverse to the axis. A bonding agent capable of bonding to the polypropylene and to the secondary covering is interposed at least between the edge and the polypropylene covering. A cured deposit of thermoset resin is applied at least over the edge of the secondary covering and bonds to the outer surfaces of the polypropylene and secondary coverings. This provides the secondary covering with increased stability against displacement radially outwardly with respect to the polypropylene covering.

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SLEEVE FOR PROTECTING POLYPROPYLENE-COVERED PIPE COMPRISING BONDING AGENT.

The present invention relates to improved arrangements for providing a secondary covering on a polypropylene covered tubular article.

5 More especially, the invention is directed toward the application of a functional secondary coating over a polypropylene-coated substrate in circumstances where it is not possible to use a high shear strength adhesive that will bond to both polypropylene and the backing component
10 of the secondary coating. This is true, for example, when the backing is a heat-shrinkable crosslinked polymer derived primarily from ethylene, which would be compatible with adhesives that bond to polyethylene, but not to polypropylene. However, the invention could also be used
15 beneficially in circumstances wherein the high shear strength adhesive is compatible with both the backing of the secondary coating and with polypropylene, but the temperature required to achieve an adequate bond to the polypropylene-coated substrate would be so high as to
20 damage the coating.

The following problems arise, for example, in the provision of a heat shrinkable polyolefin sleeve on a polypropylene coated pipe in the course of completion of a pipe joint between polypropylene coated pipe sections.

25 Firstly polypropylene coatings are generally used for high temperature pipelines, and therefore require the use of joint-completion systems that will also withstand high temperatures.

30 Secondly high strength adhesives that bond to polyethylene-based polymers do not generally bond well to polypropylene.

Thirdly, currently preferred heat-shrinkable backing

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5 sheets suitable for anticorrosion applications are based on ethylene polymers or copolymers. Polypropylene is not crosslinkable by preferred conventional methods, and there are currently therefore no commercial heat-shrinkable polypropylene backing sheets available.

10 Fourthly, those adhesives that bond well to both polypropylene and ethylene-based polymers are relatively low strength mastics or hybrid mastic/hot melt adhesives. These have excellent sealing properties, but inadequate shear resistance at elevated temperatures.

Fifthly, polypropylene coatings are typically three-layer (epoxy/copolymer adhesive/polypropylene) constructions. Preheat temperatures in excess of about 200°C can severely damage the coating.

15 Similar problems may also arise in applying other polyolefin secondary coverings over a polypropylene coated pipe section, for example in applying a polyolefin patch over a holiday in the polypropylene coating.

20 According to the present invention, there is provided an elongate tubular article extending along a longitudinal axis and having a covering comprising polypropylene thereon with an outer surface, a secondary covering comprising polyolefin with an outer surface at least partially superimposed over the polypropylene covering, said
25 secondary covering having an edge with a face extending transverse said axis, a bonding agent capable of bonding to said polypropylene and secondary coverings interposed at least between said edge and said polypropylene covering, and a cured deposit of thermoset resin applied at least
30 over said edge of the secondary covering and bonding to said outer surfaces of said polypropylene and secondary coverings and providing the secondary covering with increased stability against displacement radially outwardly with respect to said polypropylene covering.

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With this arrangement, the bonding agent, which may be, for example, a mastic or hybrid mastic/hot melt adhesive, provides excellent sealing between the polypropylene and secondary covering while the cured deposit creates a strong bond between the secondary covering and the polypropylene coating. Further, the cured deposit stabilizes the edge of the secondary covering against being lifted by axial stresses, such as soil stresses or other axial forces, such as travelling over a stinger in the course of laying pipe from a lay barge in the course of underwater pipeline installation.

The invention will now be described in more detail, by way of example only, with reference to the accompanying drawings, wherein

Fig. 1 is a partially sectional view through a pipe joint in the course of application of a heat shrinkable sleeve thereto;

Fig. 2 is a partially sectional view showing the completed pipe joint; and

Fig. 3 is a partially section view showing a modified completed pipe joint.

Fig. 1 shows a partial longitudinal cross section through two pipeline sections 11 and 12 aligned along a longitudinal axis 13 and secured together at a weld joint 14. The sections 11 and 12 each carry a polypropylene coating 16 and 17 which covers the pipe 11 or 12 along its entire length except for a short section exposed at each end of the pipe to permit the above mentioned welding operation.

Fig. 1 shows a sleeve-form protective covering 18 to be applied over the pipe weld area. The covering 18 is of sufficient length that it overlaps at each end on the

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coating 16 and 17. In the preferred form, the covering 18 comprises a heat shrinkable backing 19 provided on its underside with a functional coating 21 which is typically a sealant or adhesive. In the course of installation, the
5 backing 19 is heated so that it shrinks down tightly onto the coating 16 and 17. Usually, the fluidity and tackiness of the functional coating 21 increases as the backing 19 becomes hotter, so that the functional coating tends to wet and coat the exposed surfaces of the metal pipes 11 and 12
10 and form a tight seal on the adjacent ends of the coatings 16 and 17. The intimacy of the contact between the functional coating material 21 and the underlying surfaces is enhanced by the hoop stress imparted by the sleeve backing 19 as it shrinks down. Such sleeve 18 may be of
15 the cylindrical or wrap-around type. Many forms of heat shrinkable sleeve are known to those of ordinary skill in the art, and it is contemplated that the present invention may be used with all such sleeve.

Merely by way of example, various forms of backing and
20 functional coating are described in U.S. Pat. Nos. 4,472,468 (Tailor et al), 5,134,000 (Smythe et al), 5,175,032 (Steele et al) and 5,411,777 (Steele et al). Reference should be made to these for disclosures of suitable sleeves for use in connection with the present
25 invention.

In preferred forms, for example, the backing sheet 19 may comprise a cross-linked polyolefin sheet. Presently preferred polyolefin materials comprise blends of polyethylene with suitable copolymers such as, for example,
30 poly(ethylene-vinyl acetate), poly(ethylene-ethyl acrylate), poly(ethylene-maleic anhydride) and poly(ethylene-vinyl acetate-maleic anhydride). However, the backing sheet 19 may comprise other materials and may comprise polypropylene. Blends which aid in attaining
35 adhesion to the curable thermosetting composition are preferred.

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The functional coating 21 may comprise a mastic, hot melt adhesive or a hybrid thereof. These materials are well known to those of ordinary skill in the art, and need not be described in detail herein.

5 Preferably, the functional coating 21 is a very high shear strength hot-melt adhesive, desirably having a shear strength as measured by ASTM D1002 at the operating temperature of the article of at least about 20 psi, more desirably at least about 100 psi. Examples of suitable
10 high shear strength adhesives are the adhesive used on the heat shrinkable sleeve GTS-HT®, sold by Canusa-CPS division of Shaw Industries Ltd., and the adhesive used on the heat-shrinkable sleeve WPC-120®, produced by Raychem Corporation.

15 Before the sleeve 18 is shrunk down onto the pipe joint area, a bonding agent capable of bonding to the backing 19 as well as to the polypropylene coatings 16 and 17 is interposed between the end edges of the sleeve 19 and the coating 16 and 17. The bonding agent, indicated at 22
20 and 23 in the accompanying drawings is preferably a mastic. Usually, the mastic materials comprise substantially amorphous natural or synthetic polymers, or mixtures thereof, in contrast to the hot melt adhesive materials, which typically exhibit marked crystallinity.

25 Examples of typical mastic compositions include blends of substantially amorphous rubber materials, such as butyl rubber, natural rubber, latex SBR rubber, with tackifying resins, such as synthetic hydrocarbon tackifying resins, rosin ester tackifying resins, and inert fillers such as
30 calcium carbonate, talc and carbon black, usually together with antioxidants, and with or without admixtures of other amorphous natural or synthetic polymers, such as asphalt, polybutene and amorphous polyolefins, such as amorphous polypropylene, styrene-isoprene copolymers, and liquid
35 butyl polymers. Such mastic compositions provide excellent

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properties of excluding ingress of water to the sealed area, and, as compared with hot melt adhesive and other functional coating materials, exhibit broader softening temperatures and substantial surface tack which contribute to considerably greater ease of application over a wide range of ambient temperature including very low ambient temperatures.

The bonding agent may be a conventional mastic-hot melt adhesive hybrid.

10 The mastic and hybrid materials bond well to polypropylene and other polyolefins, as well as to hot melt adhesives, and therefore form a strong water excluding bond between the polypropylene coatings 16 and 17 and the adjacent ends of the sleeve 18.

15 The mastic portions 22 and 23 may be provided by, for example, applying a mastic tape circumferentially around the polypropylene coating 16 and 17 at the locations as indicated in Fig. 1, in register with the inner marginal portions of the sleeve 18. The mastic may be applied as a narrow band, leaving contact between adhesive 21 and coating 16 and 17, or preferably may be applied in sufficient width to cover all of the coating 16 and 17 which would otherwise come into contact with the adhesive 21, as shown in Figure 3. This ensures there is no unbonded, unsealed boundary between the polypropylene coating and the sleeve 18.

30 In installation of the sleeve 18, in its preferred use, the sleeve 18 is heated in known manner to cause it to shrink down tightly onto the polypropylene coated pipe sections as seen in Figs. 2 and 3. The adhesive 21 bonds very well to the bare surface of the steel pipe 11 and 12, but cannot bond to the polypropylene pipe coatings 16 and 17. The layer of mastic or other bonding agent 22 and 23 which, as seen in Figs. 2 and 3 on shrinking down of the

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sleeve 18 may tend to be extruded somewhat outwardly from the ends of the sleeve 18, creates a weak but water-resistant bond between the sleeve 18 and the coating 16 and 17. However, where the adhesive 21 is in contact with the coatings 16 and 17, as in Fig. 2, there is effectively no bond. As installed, the sleeve 18 cannot move as a whole because of the high shear bond between the steel pipe 11 and 12 and the sleeve 18, but the ends are susceptible to lifting. To overcome this, the ends of the sleeve 18 and the adjacent pipe coating 16 and 17 are over-coated with a layer of a hard, tough curable coating comprising a thermoset resin 24 and 26. In the examples illustrated, the composition 24 and 26 extends in the form of bands extending around the ends of the sleeve 18 and onto the adjacent surfaces of the pipe coating 16 and 17.

The curable composition is preferably applied, for example by brushing or spraying, in sufficient thickness so that, in the cured state, as seen in Figs. 2 and 3, the bands 24 and 26 of the cured deposit extend continuously from the surface of the coatings 16 and 17 continuously to at least the outer surface of the backing sheet 19, and preferably above this surface, as seen in Fig. 2, so that, in effect, the cured deposit 24 and 26 forms a solid block or abutment extending over the full depth of the end surface of the backing sheet 19. Alternatively, the curable composition may be applied in the form of a tape of fibre mesh, weave or roving impregnated with the curable composition in uncured or partially cured (B-staged) form.

On curing, the thermoset material 24 and 26 creates a strong bond between the sleeve 18 and the polypropylene coatings 16 and 17. Further, the material 24 and 26 stabilizes the end portions of the sleeve 18, which would otherwise be bonded to the polypropylene coating 16 and 17 only by the low shear mastic or other bonding agent. This guards against the ends of the sleeve 18 being lifted radially outwardly by soil stress or by other forces, such

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as travelling over the stinger of a lay barge.

In prolonged service, the thermoset composition 24 and 26 may crack or may in itself become incapable of providing a water-tight seal. In such condition, however, the

5 thermoset material 24 and 26 continues to bond the ends of the sleeve 18 to the polypropylene coating 16 and 17, and continues to safeguard the integrity of the mastic or other bonding agent 22 and 23, so that the latter continues to maintain its function in providing a water tight seal.

10 In the preferred form, the thermoset material, in its cured condition exhibits a flexural modulus (as measured by ASTM D790) of at least about 10^3 psi. Thermoset materials having a flexural modulus substantially less than about 10^3 psi tend to have insufficient stiffness to withstand the

15 pressures generated by gross soil movements. Generally speaking, the stiffer and harder the thermoset material is, the better it will withstand external stresses. However, the use of thermoset materials having a flexural modulus in excess of about 10^7 psi does not appear to significantly

20 increase the stability of the covering such as the sleeve 16, and may require use of thermosetting materials which are highly filled, excessively expensive and difficult to work with. More preferably, the flexural modulus is in the range about 10^4 psi to about 10^6 psi, still more preferably

25 about 5×10^4 psi to about 7.5×10^5 psi.

Desirably, the thermoset material has a shear strength (as measured by ASTM D 1002) of at least about 250 psi at the maximum operating temperature which the coverings are destined to encounter when the covered article is in

30 service. Materials having a shear strength significantly less than about 250 psi tend to have insufficient strength to withstand soil stresses such as may typically be encountered in pipeline service. The higher the shear strength, the better the material will perform, but the use

35 of materials having shear strengths in excess of the shear

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strength of the bond between the thermoset deposit and the first covering (typically up to about 20,000 psi) do not contribute significantly to increased resistance to soil stresses, and may involve the use of highly reinforced or
5 excessively expensive materials. More preferably, the shear strength at the maximum operating temperature is in the range about 500 to about 10,000 psi, still more preferably about 1000 to about 5000 psi.

Since, essentially, the present invention utilizes the
10 physical properties of the thermoset material, the nature of the thermoset material is not especially critical provided that it forms a bond of sufficient strength to the first and second coverings to be able to resist peeling, shearing and other stresses in service so as to improve the
15 stability of the second coverings to be able to resist peeling, shearing and other stresses in service so as to improve the stability of the second covering against displacement relative to the first covering. The thermosetting material in its uncured condition should be
20 sufficiently mobile or fluid, usually liquid or paste-like that it can be readily applied to provide the deposit having the required thickness along and preferably bridging over the edges of the sleeve 18 and the adjacent portions of the coatings 16 and 17. Desirably, the composition in
25 its uncured state has a certain degree of thixotropy so that the applied composition does not tend to flow down to a lower portion of the pipeline surface before curing. If necessary or desirable, the thermosetting composition may be modified by addition of thixotroping agents, reinforcing
30 fillers and the like.

If the thermosetting composition is applied in the form of an impregnated tape, the impregnation may take place prior to, during, or after wrapping. For example, the curable composition may be applied thickly to the
35 appropriate regions and the fibrous tape applied over it, after which the liquid curable composition is worked into

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the tape. Alternatively, the tape may be saturated with the liquid curable composition, then wrapped over the appropriate regions. One particularly preferable method is to use a fibrous tape impregnated with a moisture-activated resin, such as for example Master Wrap, which is sold by Patchmasters International Inc. The tape is first soaked in water, then wrapped on in one or more layers, with cure taking about 1 hour. Another preferred product is a fibreglass tape impregnated with a partially cured (or "B-staged") resin. After wrapping, the tape is gently heated to effect final cure.

It is contemplated that any thermosetting composition which is sufficiently mobile and fluid in its uncured state for application in the manner above described, and which, in the cured condition has the hardness and shear strength discussed above, and which can be made to bond well to each of the substrates it contacts may be used in the present invention. For example, thermosetting polyesters, polyurethanes, epoxy resins, silicone resins and polyurea resins may be employed. The presently preferred materials are epoxy resins based on bisphenol A-epichlorohydrins and cured with reactive hardeners such as primary or secondary amines. Other thermosetting compositions which may be used in the present invention will be readily apparent to those skilled in the art, and need not be described in detail herein. For example, U.S. Pat. No. 4,732,632 in the name Pieslak et al describe numerous epoxy resin compositions, and may be referred to for its disclosure of resin compositions suitable for use in the present invention. Generally, the thermosetting compositions will comprise two components, namely a resin composition and a hardener which are mixed together shortly before application. in the preferred form, the thermosetting resin composition is applied, for example by brushing or spraying, to form the bands on the ends of the sleeve such as a sleeve directly after heat shrinking of the sleeve, and while the sleeve is still hot, typically at a temperature of about

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80°C., and is allowed to cure.

Preferably, the surfaces of the polypropylene coating 16 and 17 outwardly beyond the sleeve 18 are oxidized or otherwise treated so that they will bond more strongly to the curable composition. Such methods of modifying the surface of polypropylene are well known to those skilled in the art, and are used commonly in the printing of polypropylene films and articles. The coating 16 and 17 may be oxidized by, for example, playing on their surfaces the flame of a gas torch used for heating and shrinking down the sleeve 18, or by using a hot air blower, or the surfaces may be oxidized chemically, for example through application of chromic acid solution.

The end surfaces of the sleeve 18 on which the curable composition 24 and 26 is applied tend to be oxidized as a result of the normal surface oxidation that occurs during the shrinking operation, and therefore are receptive to forming a strong bond with the curable compositions.

As will be appreciated, the principals of the invention described above may be applied in the application of other secondary coverings on a polypropylene coated article, such as, for example, in the application of a polyolefin patch on a polypropylene coated pipe. In such a case, a central portion of the patch may be adhered to a holiday with a high shear hot melt adhesive, and mastic or like bonding agent may be applied on the underside of the margin of the patch, and the edges of the patch and the adjacent surfaces of the polypropylene coating may be covered with curable thermoset composition.

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CLAIM:

1. An elongate tubular article extending along a longitudinal axis and having a covering comprising polypropylene thereon with an outer surface, a secondary
5 covering comprising polyolefin with an outer surface at least partially superimposed over the polypropylene covering, said secondary covering having an edge with a face extending transverse said axis, a bonding agent capable of bonding to said polypropylene and secondary
10 coverings interposed at least between said edge and said polypropylene covering, and a cured deposit of thermoset resin applied at least over said edge of the secondary covering and bonding to said outer surfaces of said polypropylene and secondary coverings and providing the
15 secondary covering with increased stability against displacement radially outwardly with respect to said polypropylene covering.
2. An article as claimed in claim 1 wherein the secondary covering has a functional coating on an underside applied
20 on the polypropylene covering.
3. An article as claimed in claim 2 wherein the functional coating is a very high shear strength hot melt adhesive.
4. An article as claimed in claim 3 wherein the
25 functional coating has a shear strength of at least about 20 psi.
5. An article as claimed in claim 4 wherein the shear strength is at least about 100 psi.
6. An article as claimed in claim 1 wherein the bonding
30 agent is a mastic or a mastic/hot melt adhesive hybrid.
7. An article as claimed in claim 1 wherein said deposit

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has a flexural modulus of about 10^3 to about 10^7 psi.

8. An article as claimed in claim 7 wherein said flexural modulus is about 10^4 to about 10^6 psi.

9. An article as claimed in claim 8 wherein said flexural
5 modulus is about 5×10^4 to about 7.5×10^5 psi.

10. An article as claimed in claim 1 wherein said deposit has a shear strength about 250 psi to about 20,000 psi.

11. An article as claimed in claim 10 wherein said shear strength is about 500 psi to about 10,000 psi.

10 12. An article as claimed in claim 11 wherein said shear strength is about 1000 psi to about 5000 psi.

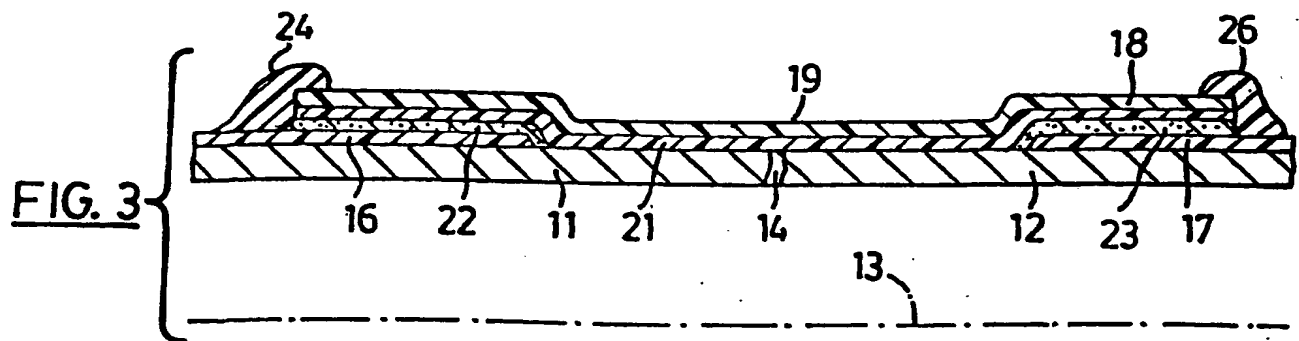
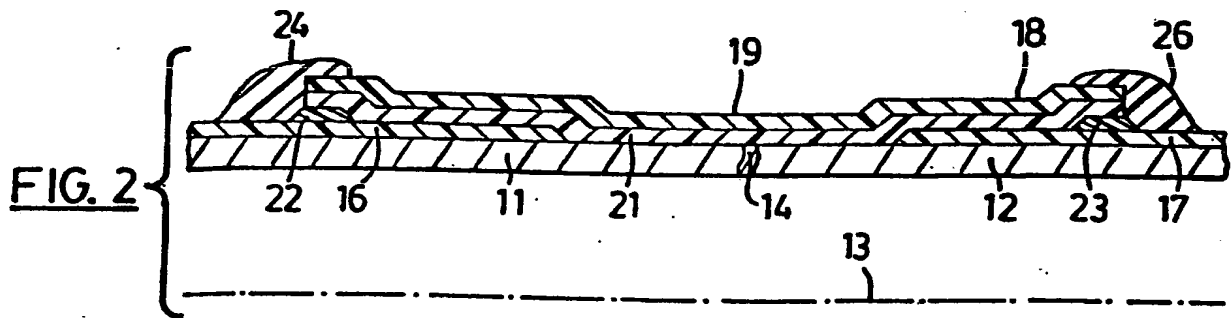
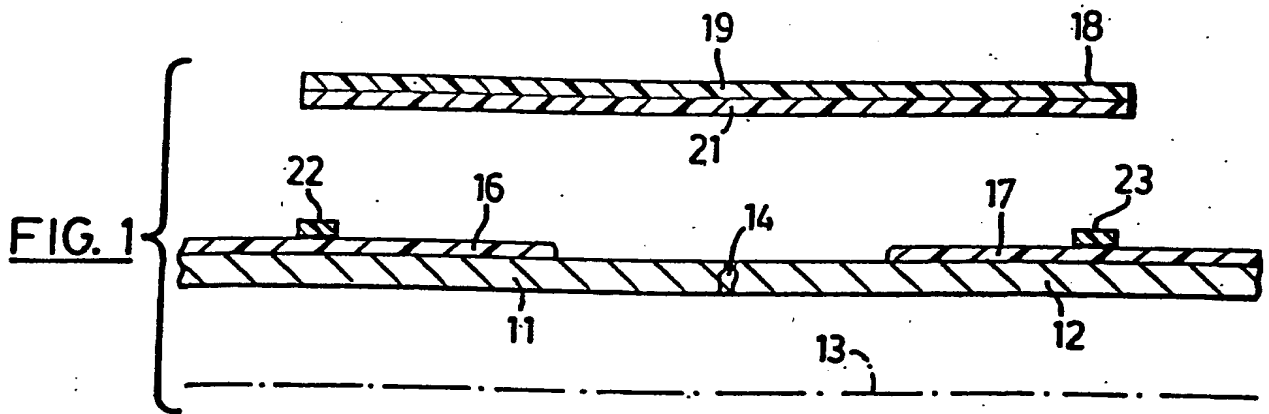
13. An article as claimed in claim 1 wherein said cured thermoset deposit comprises an epoxy resin, a polyester resin, a polyurethane resin, a silicone resin or a polyurea
15 resin.

14. An article as claimed in claim 1 wherein said secondary covering comprises sheet material and said covering has a thickness around the margins of the covering at least equal to the thickness of the sheet material.

20 15. An article as claimed in claim 1 wherein said secondary covering comprises a sleeve or a patch.

16. An article as claimed in claim 1 wherein said deposit is applied as a fibrous tape impregnated with a curable resin composition.

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INTERNATIONAL SEARCH REPORT

International Application No

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B32B1/08 F16L55/168 F16L58/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B32B F16L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	page 1, line 32 -page 2, line 33 page 4, line 1 -page 7, line 7 page 8, line 32 -page 9, line 31 page 10, line 16-32 figures 1,3	2-5
Y	EP 0 188 363 A (SHAW IND LTD) 23 July 1986 (1986-07-23) page 4, line 3-11 page 8, line 5-19 page 16, line 28 -page 17, line 19 claims 1,3-5 figure 1	2-5
	-/-	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
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- *P* document published prior to the international filing date but later than the priority date claimed

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- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

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Stabel, A

INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	WO 99 56055 A (RAYCHEM LTD ;JOHN ROBIN (GB)) 4 November 1999 (1999-11-04) column 3, paragraph 3 -column 5, paragraph 1 figures 1,2 -----	1

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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